Chapter 4
Mercury in Tributaries

4.1 Results

From March 29, 1994 to October 31, 1995, samples were collected from 11 tributaries that flow into Lake Michigan (Figure 2-3 in Chapter 2). Samples were collected as described in Section 2.4.2 and analyzed for total and dissolved mercury by cold-vapor atomic fluorescence spectrometry (see Section 2.5.2). A total of 346 samples were collected and analyzed for dissolved mercury, and 353 samples were collected and analyzed for total mercury (Table 4-1). In addition to the analysis of total and dissolved mercury, a subset of samples was analyzed for methylmercury using a combination of distillation, ethylation, gas chromatography, and cold-vapor atomic fluorescence spectrometry. A total of 203 samples were analyzed for total methylmercury, and 204 samples were analyzed for dissolved methylmercury.

Table 4-1. Number of Tributary Samples Analyzed for Mercury and Methylmercury

Analyte	Tributary	Sampling Dates	Number of Samples Analyzed		Total Number of Samples Analyzed
			Dissolved Fraction	Total Fraction	
Mercury	Fox	04/07/94 to 10/12/95	38	39	77
	Grand Calumet	08/04/94 to 10/18/95	15	15	30
	Grand	04/11/94 to 10/31/95	46	47	93
	Kalamazoo	04/12/94 to 10/30/95	38	38	76
	Manistique	04/11/94 to 10/26/95	27	27	54
	Menominee	04/13/94 to 10/11/95	23	25	48
	Milwaukee	03/29/94 to 10/06/95	36	38	74
	Muskegon	04/14/94 to 10/17/95	27	27	54
	Pere Marquette	04/05/94 to 10/18/95	28	28	56
	Sheboygan	04/06/94 to 09/19/95	35	36	71
	St. Joseph	04/06/94 to 10/27/95	33	33	66
		Total	346	353	699
Methylmercury	Fox	01/11/95 to 08/30/95	17	15	32
	Grand Calumet	02/13/95 to 10/18/95	7	8	15
	Grand	04/28/94 to 10/31/95	31	33	64
	Kalamazoo	01/26/95 to 10/30/95	16	14	30
	Manistique	04/11/94 to 10/26/95	20	21	41
	Menominee	01/17/95 to 10/11/95	12	12	24
	Milwaukee	01/10/95 to 10/06/95	21	21	42
	Muskegon	01/24/95 to 10/17/95	11	11	22
	Pere Marquette	04/05/94 to 10/18/95	22	20	42
	Sheboygan	04/14/94 to 10/24/95	32	32	64
	St. Joseph	01/27/95 to 10/27/95	15	16	31
		Total	204	203	407

4.1.1 Geographical Variation

4.1.1.1 Mercury

Total mercury concentrations measured in Lake Michigan tributaries ranged from 0.536 to 191 ng/L. In the 11 tributaries monitored in the LMMB Study, mean total mercury concentrations ranged from 1.07 ng/L in the Muskegon River to 28.9 ng/L in the Fox River (Table 4-2). Analysis of variance (and Tukey's pairwise comparison test) revealed that total mercury concentrations in the Fox River were significantly higher than in any other Lake Michigan tributary (Figure 4-1). The mean total mercury concentration in the Fox River was 2.7 to 27 times higher than in other Lake Michigan tributaries. The Fox River watershed has long been highly industrialized and Hurley *et al.* (1998a) have suggested that the main source of Fox River mercury loads is resuspension of contaminated sediments. Following the Fox River, total mercury concentrations were highest in the Kalamazoo and Grand Calumet Rivers. Total mercury concentrations in these tributaries were significantly higher (at the 95% confidence level) than in any other tributary, except for the Fox River. These rivers are located to the south and southeast of Lake Michigan (Figure 4-2), where urban and industrial land uses are predominant. The lowest total mercury concentrations were observed in the Muskegon, Pere Marquette, Manistique, and Menominee Rivers (Figure 4-2), which are the more northern tributaries that are primarily forested. Total mercury concentrations in the Muskegon River were significantly lower than any other Lake Michigan tributary (Figure 4-1). Hurley *et al.* (1998b) explained that the low mercury concentrations in this tributary may be due to Lake Muskegon, which is located directly upstream of the sampling site and acts as a temporary sink for contaminants.

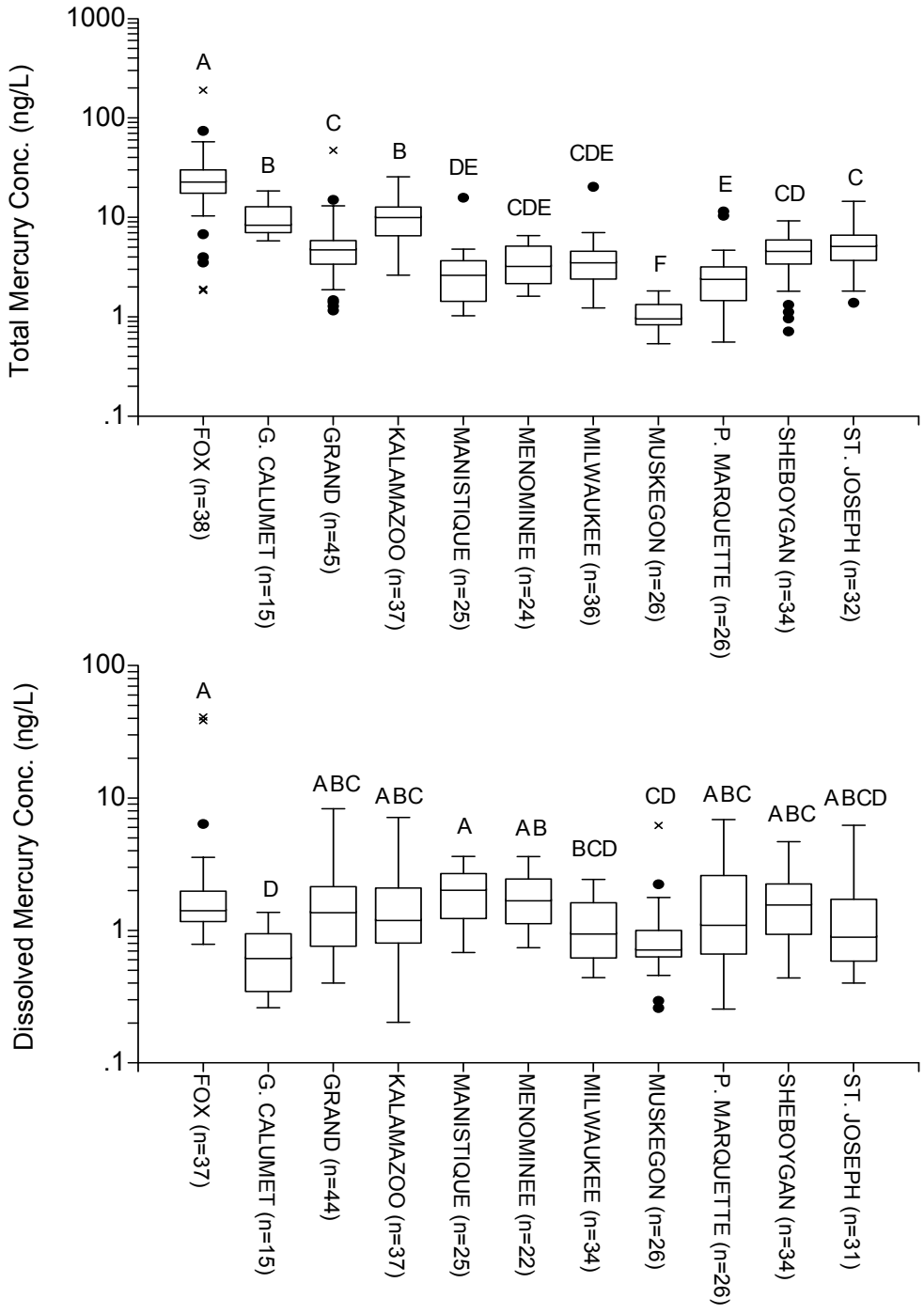
Dissolved mercury concentrations were more consistent among tributaries than total mercury concentrations. Mean dissolved mercury concentrations only ranged from 0.666 ng/L in the Grand Calumet River to 3.71 in the Fox River. The remaining tributaries all contained mean dissolved mercury levels between 1 and 2 ng/L (Table 4-2). Fewer significant differences in dissolved mercury concentrations also were seen among tributaries (Figure 4-1 and Figure 4-2). Unlike total mercury concentrations, dissolved mercury concentrations in the Fox River were not significantly higher than in all other tributaries. Dissolved mercury concentrations in the Fox River were only significantly higher than in three other tributaries (Grand Calumet, Muskegon, and Milwaukee Rivers). Following the Fox River, mean dissolved mercury concentrations were highest in the Manistique and Menominee Rivers, two tributaries that had among the lowest concentrations of total mercury. Dissolved mercury concentrations in the Manistique River were significantly higher than in three other tributaries, and dissolved mercury concentrations in the Menominee River was significantly higher than in two other tributaries. The lowest mean dissolved mercury concentration was in the Grand Calumet River, which was among the highest in total mercury concentrations. The mean dissolved mercury concentration at this site was significantly lower than in seven other tributaries.

Table 4-2. Mean Mercury Concentrations Measured in Lake Michigan Tributaries

Fraction	Tributary	N	Mean (ng/L)	Median (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	Below DL (%)
Dissolved	Fox	37	3.71	1.44	0.786 to 40.8	8.75	236	0.00
	Grand Calumet	15	0.666	0.628	0.261 to 1.37	0.341	51.2	0.00
	Grand	44	1.68	1.39	0.400 to 8.29	1.32	78.9	0.00
	Kalamazoo	37	1.62	1.22	0.202 to 7.12	1.41	87.3	0.00
	Manistique	25	1.99	2.06	0.680 to 3.61	0.815	40.9	0.00
	Menominee	22	1.87	1.71	0.739 to 3.61	0.861	46.1	0.00
	Milwaukee	34	1.15	0.963	0.439 to 2.42	0.594	51.7	0.00
	Muskegon	26	1.08	0.730	0.259 to 6.20	1.13	105	0.00
	Pere Marquette	26	1.79	1.12	0.254 to 6.86	1.56	87.0	0.00
	Sheboygan	34	1.64	1.59	0.437 to 4.68	0.928	56.5	0.00
	St. Joseph	31	1.46	0.912	0.399 to 6.21	1.42	97.2	0.00
Particulate[a]	Fox	37	25.8	22.1	-11.3 to 153	26.2	101	—
	Grand Calumet	15	9.26	8.00	4.68 to 18.2	4.34	46.9	—
	Grand	43	4.29	3.23	-3.54 to 46.6	7.16	167	—
	Kalamazoo	37	9.00	8.81	0.786 to 23.7	5.56	61.8	—
	Manistique	25	1.08	0.447	-0.0865 to 13.3	2.61	242	—
	Menominee	22	1.92	1.75	-0.339 to 4.81	1.57	81.7	—
	Milwaukee	34	2.93	2.45	-0.320 to 18.6	3.06	104	—
	Muskegon	26	-0.0058	0.215	-4.96 to 0.742	1.08	—	—
	Pere Marquette	26	1.09	0.758	-5.40 to 7.67	2.49	228	—
	Sheboygan	33	3.02	3.12	-0.0094 to 7.42	1.59	52.9	—
	St. Joseph	31	4.04	4.18	-1.73 to 9.24	2.33	57.6	—
Total	Fox	38	28.9	23.5	1.84 to 191	30.5	106	0.00
	Grand Calumet	15	9.93	8.63	5.81 to 18.5	4.29	43.2	0.00
	Grand	45	6.02	4.87	1.16 to 47.5	6.91	115	0.00
	Kalamazoo	37	10.6	10.3	2.62 to 25.7	5.77	54.3	0.00
	Manistique	25	3.07	2.71	1.02 to 15.8	2.89	94.2	0.00
	Menominee	24	3.63	3.33	1.61 to 6.57	1.57	43.3	0.00
	Milwaukee	36	4.08	3.62	1.23 to 20.3	3.19	78.1	0.00
	Muskegon	26	1.07	0.984	0.536 to 1.82	0.354	33.1	0.00
	Pere Marquette	26	2.88	2.46	0.557 to 11.5	2.59	90.1	0.00
	Sheboygan	34	4.52	4.72	0.712 to 9.25	2.00	44.1	0.00
	St. Joseph	32	5.40	5.29	1.38 to 14.5	2.70	50.1	0.00

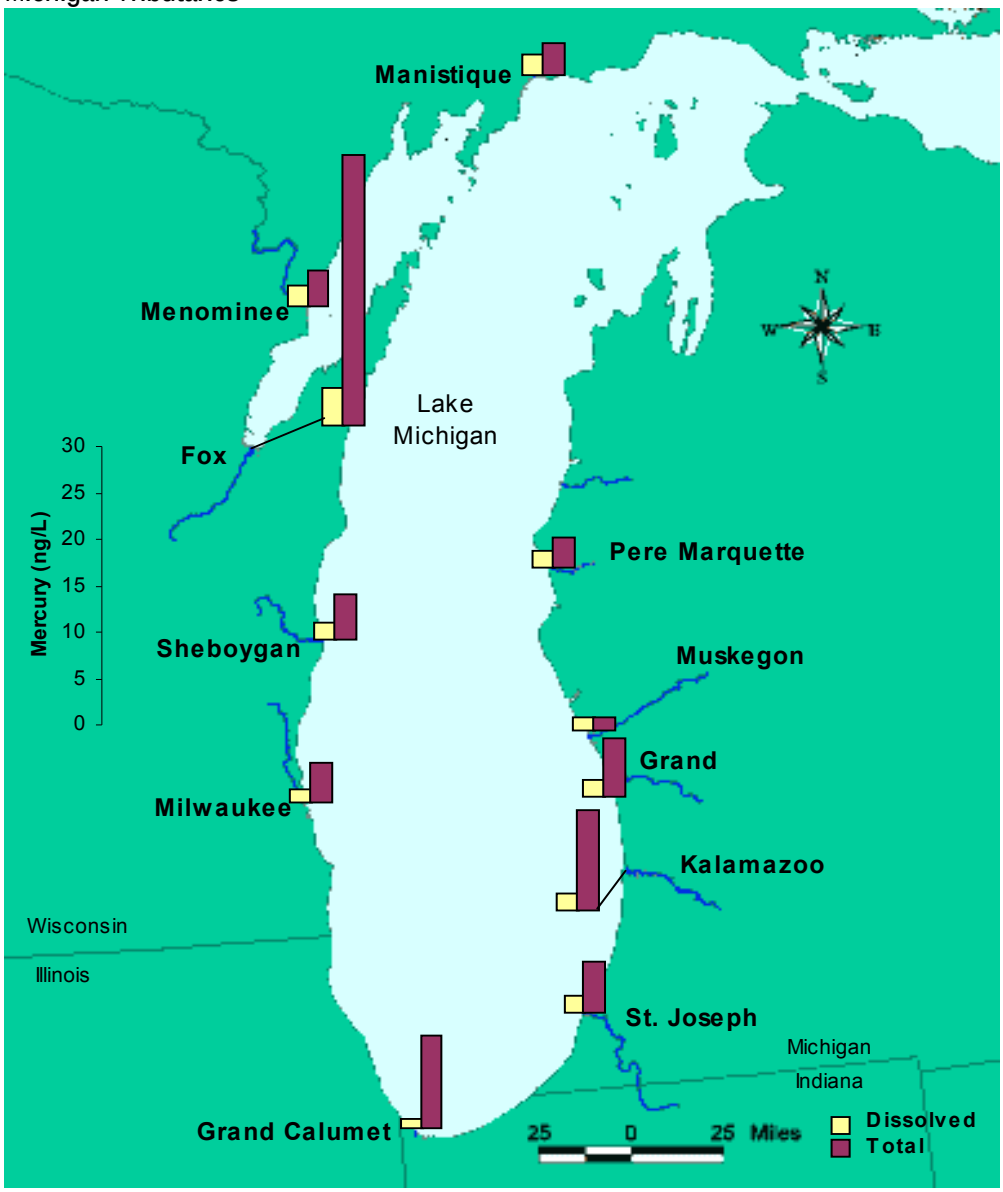
[a] Mercury concentrations in the particulate fraction were not directly measured. Particulate concentrations for each sample were calculated as the difference between the measured total and dissolved concentrations. If measured dissolved concentrations were greater than measured total concentrations, the calculated concentration in the particulate fraction was a negative number. Because particulate concentrations were calculated from two measured values, these reported concentrations will contain more variability than measured values reported for dissolved and total fractions. Also, the percent of samples below the detection limit could not be determined for the particulate fraction, because this fraction was not directly measured and detection limits for this fraction were not developed.

Figure 4-1. Total and Dissolved Mercury Concentrations in Lake Michigan Tributaries



Boxes represent the 25th (box bottom), 50th (center line), and 75th (box top) percentile results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. Xs represent results beyond 3*IQR from the box. Letters above the boxes represent results of analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05).

Figure 4-2. Mean Total and Dissolved Mercury Concentrations Measured in Lake Michigan Tributaries



4.1.1.2 Methylmercury

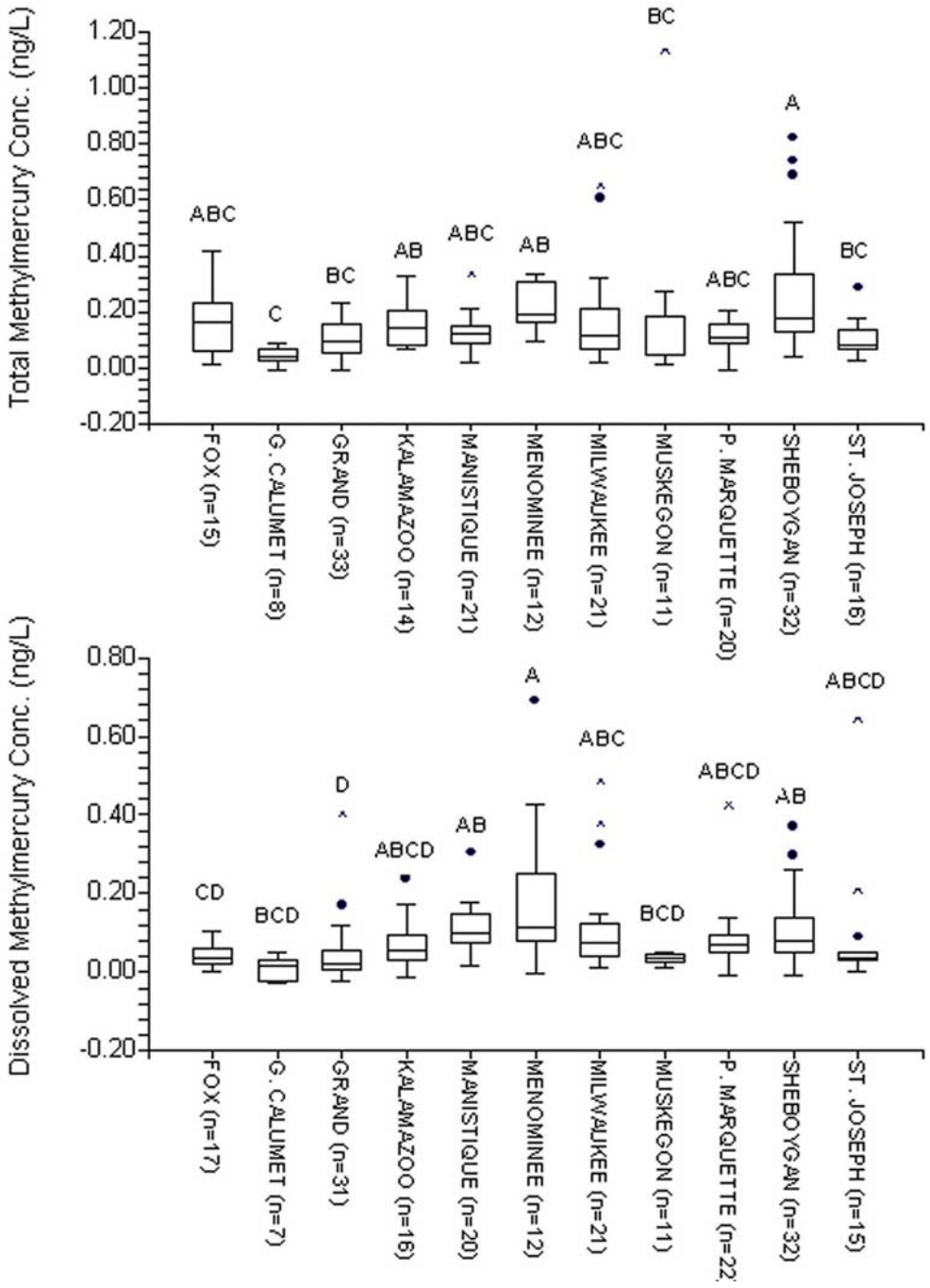
The geographical pattern of methylmercury concentrations in Lake Michigan tributaries was very different from that of total mercury. While total mercury concentrations were much higher in the Fox River than in other tributaries, methylmercury concentrations in four other tributaries were higher than in the Fox River (Table 4-3). Mean total methylmercury concentrations in Lake Michigan tributaries ranged from 0.0424 ng/L in the Grand Calumet to 0.260 ng/L in the Sheboygan River (Table 4-3). Total methylmercury concentrations in the Sheboygan River were significantly higher than in the St. Joseph, Muskegon, Grand, and Grand Calumet Rivers (Figure 4-3). Total methylmercury concentrations in the Grand Calumet were significantly lower than in the Sheboygan, Kalamazoo, and Menominee Rivers. No other significant differences in total methylmercury were observed among Lake Michigan tributaries.

Table 4-3. Mean Methylmercury Concentrations Measured in Lake Michigan Tributaries

Fraction	Tributary	N	Mean (ng/L)	Median (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	Below DL (%)
Dissolved	Fox	17	0.0419	0.0420	0.00100 to 0.103	0.0254	60.7	23.5
	Grand Calumet	7	0.0133	0.0220	-0.0281 to 0.0527	0.0300	226	42.9
	Grand	31	0.0479	0.0240	-0.0212 to 0.404	0.0779	163	41.9
	Kalamazoo	16	0.0704	0.0620	-0.0137 to 0.240	0.0649	92.3	18.8
	Manistique	20	0.114	0.106	0.0180 to 0.304	0.0624	54.6	5.00
	Menominee	12	0.182	0.117	-0.00154 to 0.692	0.198	109	8.33
	Milwaukee	21	0.115	0.0774	0.00977 to 0.487	0.126	110	4.76
	Muskegon	11	0.0363	0.0386	0.0111 to 0.0508	0.0128	35.2	9.09
	Pere Marquette	22	0.0850	0.0733	-0.00700 to 0.428	0.0839	98.6	9.09
	Sheboygan	32	0.106	0.0860	-0.00868 to 0.371	0.0848	79.7	3.13
	St. Joseph	15	0.0915	0.0393	0.000980 to 0.645	0.161	175	6.67
Particulate[a]	Fox	15	0.118	0.134	-0.0300 to 0.398	0.115	97.8	—
	Grand Calumet	7	0.0309	0.0274	-0.0162 to 0.112	0.0494	160	—
	Grand	29	0.0492	0.0500	-0.225 to 0.172	0.0762	155	—
	Kalamazoo	14	0.0809	0.0806	-0.164 to 0.344	0.115	142	—
	Manistique	19	0.0073	0.0080	-0.247 to 0.203	0.0879	1210	—
	Menominee	12	0.0351	0.0712	-0.492 to 0.268	0.214	609	—
	Milwaukee	20	0.0552	0.0370	-0.281 to 0.568	0.209	379	—
	Muskegon	11	0.148	0.0254	-0.0023 to 1.08	0.319	216	—
	Pere Marquette	20	0.0312	0.0270	-0.283 to 0.122	0.0834	268	—
	Sheboygan	29	0.139	0.0840	-0.226 to 0.767	0.193	139	—
	St. Joseph	15	0.0081	0.0474	-0.579 to 0.236	0.184	2280	—
Total	Fox	15	0.162	0.170	0.0150 to 0.413	0.106	65.3	6.67
	Grand Calumet	8	0.0424	0.0428	-0.00804 to 0.0883	0.0297	70.0	12.5
	Grand	33	0.104	0.0993	-0.00600 to 0.232	0.0593	57.0	6.06
	Kalamazoo	14	0.153	0.147	0.0647 to 0.33	0.0773	50.6	0.00
	Manistique	21	0.123	0.128	0.0210 to 0.340	0.0699	56.7	0.00
	Menominee	12	0.217	0.196	0.0971 to 0.331	0.0762	35.1	0.00
	Milwaukee	21	0.170	0.117	0.0220 to 0.651	0.170	100	0.00
	Muskegon	11	0.184	0.0537	0.00881 to 1.13	0.323	176	9.09
	Pere Marquette	20	0.116	0.110	-0.00796 to 0.202	0.0514	44.4	5.00
	Sheboygan	32	0.260	0.182	0.038 to 0.822	0.206	79.1	0.00
	St. Joseph	16	0.103	0.0846	0.0252 to 0.286	0.0639	61.8	0.00

[a] Mercury concentrations in the particulate fraction were not directly measured. Particulate concentrations for each sample were calculated as the difference between the measured total and dissolved concentrations. If measured dissolved concentrations were greater than measured total concentrations, the calculated concentration in the particulate fraction was a negative number. Because particulate concentrations were calculated from two measured values, these reported concentrations will contain more variability than measured values reported for dissolved and total fractions. Also, the percent of samples below the detection limit could not be determined for the particulate fraction, because this fraction was not directly measured and detection limits for this fraction were not developed.

Figure 4-3. Total and Dissolved Methylmercury Concentrations in Lake Michigan Tributaries



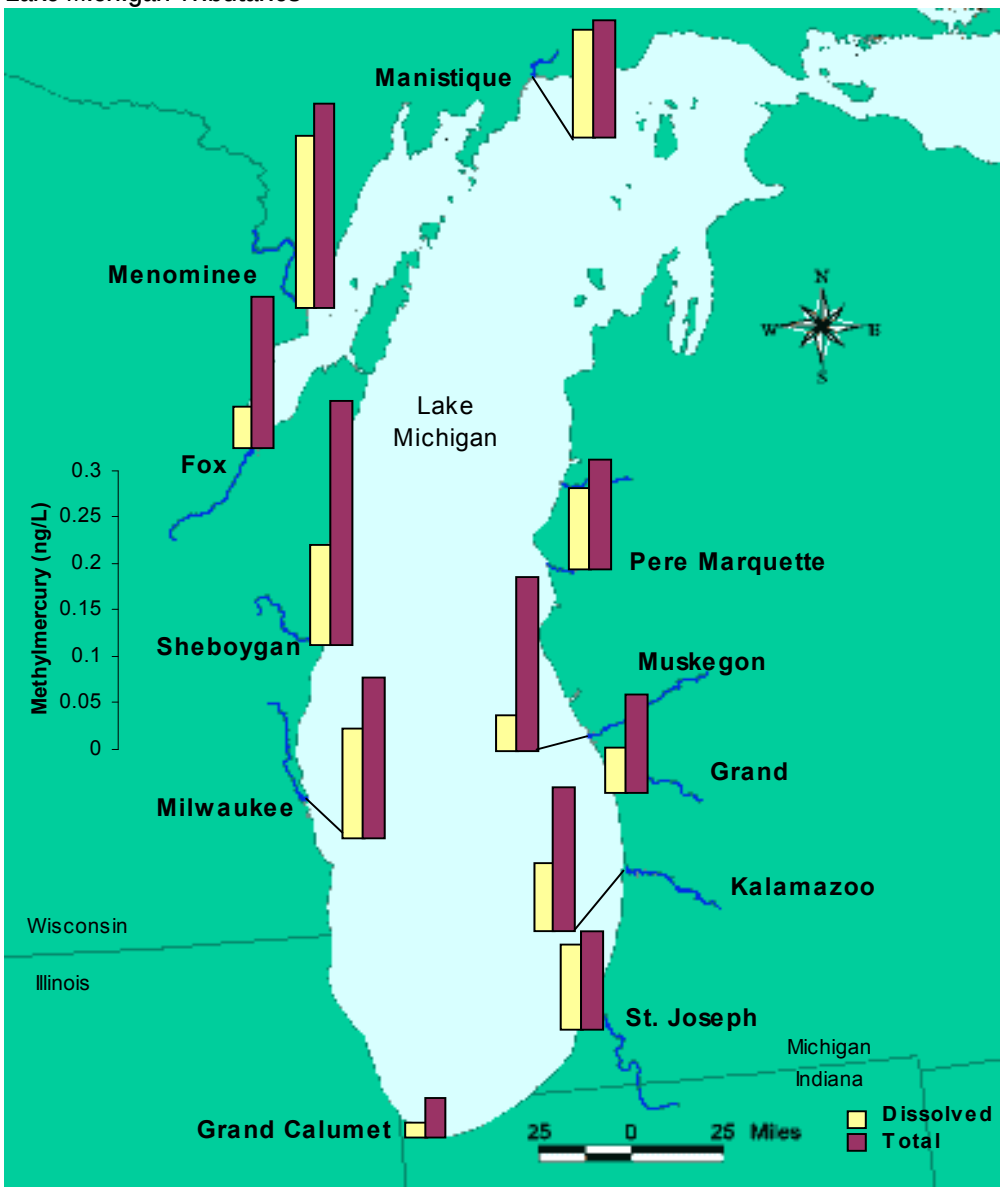
Boxes represent the 25th (box bottom), 50th (center line), and 75th (box top) percentile results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. Xs represent results beyond 3*IQR from the box. Letters above the boxes represent results of analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05).

The geographical pattern of dissolved methylmercury concentrations in Lake Michigan tributaries also were different from that of dissolved mercury. Mean dissolved methylmercury concentrations ranged from 0.0133 ng/L in the Grand Calumet to 0.182 ng/L in the Menominee River. Dissolved

methylmercury concentrations in the Menominee were significantly higher than in the Muskegon, Fox, Grand, and Grand Calumet Rivers. Dissolved methylmercury concentrations in the Sheboygan and Manistique Rivers were significantly higher than in the Fox and Grand Rivers, and dissolved methylmercury concentrations in the Milwaukee River were significantly higher than in the Grand River.

While the more northern and forested watersheds had lower total mercury concentrations, these tributaries did not have corresponding lower concentrations of methylmercury (Figure 4-4). Methylmercury concentrations in the Manistique, Menominee, Pere Marquette, and Muskegon Rivers were not significantly lower than in any other sites, with the exception of the Muskegon River being significantly lower than the Sheboygan River in total methylmercury. Similarly, those industrialized sites that had the highest total mercury levels (Fox, Kalamazoo, and Grand Calumet Rivers), did not have corresponding high methylmercury concentrations. Total methylmercury concentrations in these tributaries were not significantly higher than in any other site.

Figure 4-4. Mean Total and Dissolved Methylmercury Concentrations Measured in Lake Michigan Tributaries



4.1.2 Seasonal Variation

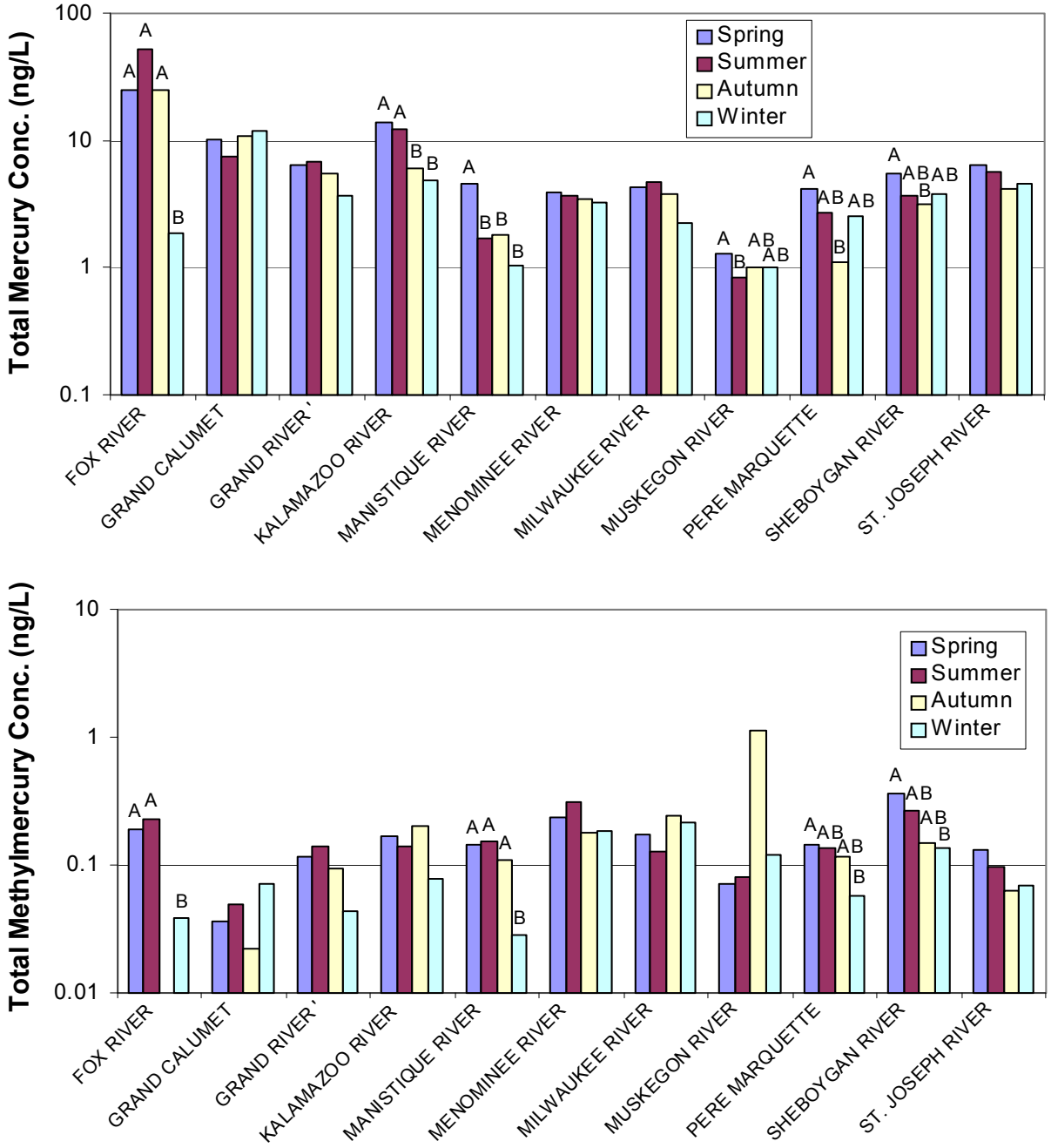
Tributary samples were collected for mercury analysis throughout seven consecutive seasons (Spring 1994 through Autumn 1995). Analysis of variance (with Tukey's pairwise comparison test) revealed that total mercury concentrations differed significantly among season in six of the eleven tributaries (Figure 4-5). In the Fox River, winter total mercury concentrations were significantly lower than in any other season. In the Kalamazoo River, winter and autumn concentrations of total mercury were significantly lower than spring or summer concentrations. In the Manistique River, spring concentrations of total mercury were significantly higher than in other seasons. In the Muskegon River, spring total mercury concentrations were significantly higher than summer concentrations. In the Pere Marquette and Sheboygan Rivers, spring total mercury concentrations were significantly higher than concentrations during autumn.

While seasonal patterns varied among tributaries, total mercury concentrations were generally higher in the spring and lower in the winter. Spring concentrations of total mercury were higher than winter values in ten of the eleven tributaries, and these differences were statistically significant in three of the tributaries. In all six tributaries that showed significant seasonal differences, total mercury concentrations were significantly higher in the spring than in other seasons.

Methylmercury concentrations differed significantly among seasons in four tributaries (Figure 4-5). In the Fox and Manistique Rivers, total methylmercury concentrations during the winter were significantly lower than in all other seasons. In the Pere Marquette and Sheboygan Rivers, total methylmercury concentrations during the winter were significantly lower than in the spring. Similar to total mercury concentrations, total methylmercury concentrations were generally higher in the spring and lower in the winter. Spring concentrations of total methylmercury were higher than winter values in eight of eleven tributaries and these differences were statistically significant in four of these tributaries.

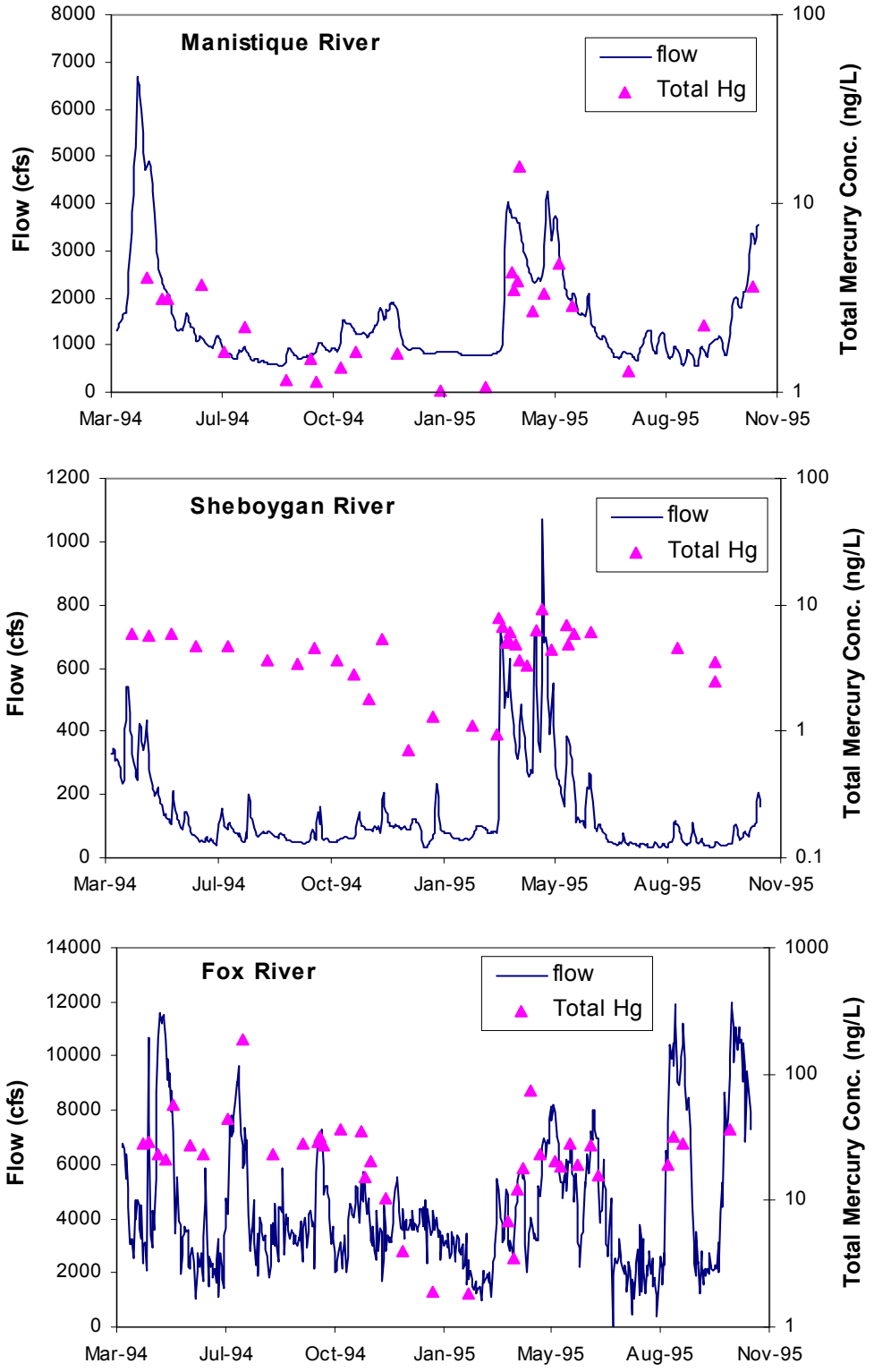
In most of the tributaries with significant seasonal differences in total mercury and methylmercury concentrations, difference were tied to the seasonal flow regimes of the tributaries. The flow regimes of many of these tributaries were dominated by high spring flows, which coincided with higher mercury concentrations. Low mercury concentrations in the winter also coincided with lower tributary flows. Figure 4-6 demonstrates this effect in the Manistique, Sheboygan, and Fox Rivers. Ice cover in the winter in many of these tributaries may also lead to reduced mixing and resuspension of contaminated sediments, which would result in lower total mercury concentrations during the winter. The hydrograph for the Fox River also demonstrates that high mercury concentrations are often associated with peak flow events throughout the year. Many of the highest total mercury concentrations measured in the Fox River coincided with high storm event flows. Indeed, tributary mercury concentrations were correlated with flow in many of the tributaries (see Section 4.1.3).

Figure 4-5. Seasonal Variation of Mercury Concentrations in Lake Michigan Tributaries



Bars with the same letter were not statistically different (at alpha = 0.05).

Figure 4-6. Seasonal Flow Patterns and Total Mercury Concentrations in Selected Lake Michigan Tributaries



4.1.3 Other Factors Affecting Tributary Mercury Concentrations

As previously mentioned (see Section 4.1.2), peaks in mercury concentrations in some tributaries coincided with either spring high flow conditions or high flows related to storm events. Significant positive correlations existed between flow and total mercury concentrations (both log transformed) in six tributaries (the Fox, Grand, Sheboygan, Milwaukee, Menominee, and Manistique Rivers). In these six tributaries, r^2 values indicated that flow accounted for 17 to 65% of the variability in total mercury concentrations (Table 4-4). For methylmercury, only two tributaries (the Fox and Menominee Rivers) exhibited significant positive correlations with flow.

Table 4-4. Correlation of Tributary Mercury Levels with Tributary Flow

Fraction	Tributary	N	Correlation Coefficient	r^2	p-value
Total Mercury	Fox	38	0.417	0.174	0.0091
	Grand	45	0.431	0.185	0.0032
	Grand Calumet	13	0.311	0.0965	0.302
	Kalamazoo	37	-0.0729	0.00532	0.668
	Manistique	25	0.806	0.649	<0.0001
	Menominee	24	0.662	0.438	0.0004
	Milwaukee	36	0.656	0.430	<0.0001
	Muskegon	26	0.258	0.0666	0.203
	Pere Marquette	26	0.271	0.0732	0.181
	Sheboygan	34	0.595	0.354	0.0002
	St. Joseph	32	0.136	0.0185	0.458
Total Methylmercury	Fox	15	0.579	0.335	0.0238
	Grand	31	-0.00648	0.0000410	0.972
	Grand Calumet	7	-0.0705	0.00497	0.881
	Kalamazoo	14	-0.313	0.0980	0.276
	Manistique	21	0.344	0.118	0.127
	Menominee	12	0.589	0.347	0.0440
	Milwaukee	21	0.357	0.128	0.112
	Muskegon	11	-0.273	0.0743	0.418
	Pere Marquette	19	-0.227	0.0517	0.349
	Sheboygan	32	0.310	0.0963	0.0838
	St. Joseph	16	0.285	0.0811	0.285

Because most of the mercury in the water column is bound to dissolved or suspended organic matter (USEPA, 1997c), mercury concentrations are expected to correlate with measures of solids and organic carbon. In coordination with tributary sampling of mercury, samples also were analyzed for dissolved organic carbon (DOC), particulate organic carbon (POC), and total solids (TS). Four of the eleven tributaries showed significant positive correlations between total mercury and DOC concentrations (Table 4-5). Seven tributaries showed significant positive correlations between total mercury and POC concentrations. In these seven tributaries, POC accounted for 23 to 62% of the variability in total mercury concentrations. The strongest correlations, however, were between TS and total mercury concentrations. All but the Muskegon River exhibited significant positive correlations between TS and total mercury. Total solids accounted for up to 82% of the variability in total mercury concentrations. It is possible that the POC and DOC correlations were auto-correlations, due to the attachment of not only mercury, but also POC and DOC, to the total solids.

Table 4-5. Correlations of Total Mercury Levels in Lake Michigan Tributaries with Dissolved Organic Matter (DOC), Particulate Organic Matter (POC), and Total Solids (TS)

Analyte	Tributary	N	Correlation Coefficient	r^2	p-value
DOC	Fox	38	-0.221	0.0488	0.182
	Grand	42	0.341	0.116	0.0273
	Grand Calumet	15	0.463	0.215	0.0820
	Kalamazoo	34	0.221	0.0488	0.209
	Manistique	24	0.531	0.282	0.0076
	Menominee	22	0.281	0.0791	0.205
	Milwaukee	34	0.511	0.261	0.0020
	Muskegon	26	-0.192	0.0368	0.348
	Pere Marquette	26	0.259	0.0670	0.202
	Sheboygan	33	0.676	0.457	<0.0001
	St. Joseph	31	-0.116	0.0134	0.536
POC	Fox	37	0.625	0.391	<0.0001
	Grand	42	0.220	0.0483	0.162
	Grand Calumet	13	0.776	0.602	0.0018
	Kalamazoo	33	0.0805	0.00648	0.656
	Manistique	25	0.347	0.120	0.0896
	Menoninee	23	0.500	0.250	0.0151
	Milwaukee	34	0.638	0.407	<0.0001
	Muskegon	25	-0.0868	0.00753	0.680
	Pere Marquette	26	0.651	0.424	0.0003
	Sheboygan	29	0.790	0.624	<0.0001
	St. Joseph	30	0.476	0.227	0.0078
TS	Fox	38	0.786	0.618	<0.0001
	Grand	45	0.606	0.367	<0.0001
	Grand Calumet	14	0.855	0.731	<0.0001
	Kalamazoo	36	0.817	0.668	<0.0001
	Manistique	25	0.663	0.439	0.0003
	Menominee	24	0.832	0.693	<0.0001
	Milwaukee	35	0.881	0.777	<0.0001
	Muskegon	25	-0.215	0.0464	0.301
	Pere Marquette	26	0.823	0.677	<0.0001
	Sheboygan	32	0.908	0.824	<0.0001
	St. Joseph	31	0.775	0.600	<0.0001

4.1.4 Mercury Forms

Total and dissolved fractions of mercury were directly measured in the LMMB Study, and mercury in the particulate fraction was calculated by subtraction. Tributaries varied greatly in the contribution of mercury from the dissolved and particulate fractions. Tributaries ranged from the Muskegon River, with the impact of Lake Muskegon, where virtually all of the total mercury (99%) was attributable to the

dissolved fraction, to the Grand Calumet River, where virtually all of the total mercury (92%) was attributable to the particulate fraction (Table 4-6). There was a distinct separation of tributaries that were dominated by the dissolved mercury fraction and tributaries that were dominated by the particulate mercury fraction. The Menominee, Manistique, Pere Marquette, and Muskegon Rivers were dominated by the dissolved mercury fraction. Each of these tributaries contained greater than 50% of total mercury in the dissolved fraction, and the Manistique, Pere Marquette, and Muskegon Rivers contained greater than 75% of total mercury in the dissolved fraction. These tributaries are the more northern tributaries with more forested watersheds.

The Fox, Grand Calumet, and Kalamazoo Rivers were dominated by mercury in the particulate fraction. Each of these tributaries contained more than 75% of total mercury in the particulate fraction. These three tributaries are among the most urbanized and industrialized watersheds evaluated in the study.

In addition to measurement of total and dissolved mercury, methylmercury was measured in the total and dissolved fractions. In most of the tributaries, methylmercury comprised less than 6% of the total mercury (Table 4-6). This is consistent with USEPA (1997c) reports that less than 10% of total mercury in a water column typically exists as a methylmercury complex. The one exception was the Muskegon River, where methylmercury accounted for an average of 21% of total mercury. As Hurley *et al.* (1998b) explained, Lake Muskegon is located directly upstream of the Muskegon River sampling site. This lake traps particulates and particulate-bound contaminants, which reduces the load of particulate mercury in the Muskegon River. As evidence of this, the Muskegon River had the lowest particulate mercury concentration (virtually zero), the lowest particulate organic carbon concentration (0.537 mg/L), and the lowest total solids concentration (3.04 mg/L). In addition to reducing the particulate load of mercury, Lake Muskegon could provide favorable conditions for the methylation of mercury. This could explain the much higher percentage of methylmercury in the Muskegon River than other tributaries.

Methylmercury is the bioavailable form of mercury that is readily accumulated and biomagnified in aquatic food webs. While methylmercury accounts for less than 10% of the total mercury in surface waters, methylmercury typically accounts for more than 90% of total mercury in fish tissue (Watras and Bloom, 1992).

Table 4-6. Percentages of Total Mercury Found in Various Forms

Tributary	Mean Percent of Total Mercury as [a]		
	Dissolved	Particulate	Methylmercury
Fox	15	85	0.97
Grand Calumet	8	92	0.48
Grand	43	57	2.6
Kalamazoo	19	81	2.0
Manistique	78	22	4.7
Menominee	54	46	5.3
Milwaukee	34	66	5.2
Muskegon	99	0.64	21
Pere Marquette	80	20	5.6
Sheboygan	38	62	5.9
St. Joseph	29	71	2.1

[a] The dissolved and particulate fractions are mutually exclusive and add to 100% of the total mercury. The percent of total mercury in the form of methylmercury is presented separately, however, this portion may exist in either dissolved or particulate fractions as well and is already accounted for in those fractions.

4.2 Quality Implementation and Assessment

As described in Section 1.5.5, the LMMB QA program prescribed minimum standards to which all organizations collecting data were required to adhere. The quality activities implemented for the mercury monitoring portion of the study are further described in Section 2.6 and included use of SOPs, training of laboratory and field personnel, and establishment of MQOs for study data. A detailed description of the LMMB quality assurance program is provided in *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b). A brief summary of the quality of tributary mercury and methylmercury data is provided below.

Quality Assurance Project Plans (QAPPs) were developed by the PIs and were reviewed and approved by GLNPO. Each researcher trained field personnel in sample collection SOPs prior to the start of the field season and analytical personnel in analytical SOPs prior to sample analysis. Each researcher submitted test electronic data files containing field and analytical data according to the LMMB data reporting standard prior to study data submittal. GLNPO reviewed these test data sets for compliance with the data reporting standard and provided technical assistance to the researchers. In addition, each researcher's laboratory was audited during an on-site visit at least once during the time LMMB samples were being analyzed. The auditors reported positive assessments and did not identify issues that adversely affected the quality of the data.

As discussed in Section 2.6, data verification was performed by comparing all field and QC sample results produced by each PI with their MQOs and with overall LMMB Study objectives. Analytical results were flagged when pertinent QC sample results did not meet acceptance criteria as defined by the MQOs. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. Tables 4-7 and 4-8 provide a summary of flags applied to the tributary mercury and methylmercury data, respectively. The summaries include the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but do not include all flags applied to the data to document sampling and analytical information, as discussed in Section 2.6. A total of 15 dissolved mercury and 15 total mercury samples were flagged as invalid by the PI. These samples were invalidated because they were prepared and analyzed without a Tenax TA® pretrap (see section 3.19 of USEPA 1997b) and data quality was significantly reduced. These samples were not used in any of the statistical analyses described in this report. For methylmercury, no samples were flagged invalid, and therefore, all results were used in the statistical analyses described in this chapter.

Table 4-7. Summary of Routine Field Sample Flags Applied to Mercury Data from Lake Michigan Tributaries

Flag	Number of QC samples		Percentage of Samples Flagged	
	Dissolved	Total	Dissolved	Total
INV, Invalid Result	—	—	4% (15)	4% (15)
EHT, Exceeded Holding Time	—	—	0	0
FDL, Failed Lab Duplicate	340 lab duplicate groups	347 lab duplicate groups	4% (15)	2% (6)
FFD, Failed Field Duplicate	49 field duplicate pairs	49 field duplicate pairs	3% (9)	3% (11)
FSL, Failed Lab Fortified Spike	65 lab fortified spike samples	53 lab fortified spike samples	1% (3)	1% (2)

The most frequently applied data validation flag for methylmercury data was for exceeding sample holding times. More than half of the samples analyzed for methylmercury (55% of dissolved methylmercury, and 57% of total methylmercury samples) were analyzed beyond the 2-year established

holding time. The median holding time for methylmercury samples was 1,358 days, and samples were held as long as 1,897 days prior to methylmercury analysis. The MQOs for holding times were based on educated, conservative assessments by the PIs, however, the appropriateness of these holding times have not been rigorously determined and the effects of extended holding times have not been investigated in the tributary matrix. All total and dissolved mercury samples were analyzed within the 2-year holding time, and therefore, no total or dissolved mercury results were flagged for exceeding the holding time.

Table 4-8. Summary of Routine Field Sample Flags Applied to Methylmercury Data from Lake Michigan Tributaries

Flag	Number of QC samples		Percentage of Samples Flagged	
	Dissolved	Total	Dissolved	Total
INV, Invalid Result	—	—	0	0
EHT, Exceeded Holding Time	—	—	55% (113)	57% (117)
FDL, Failed Lab Duplicate	14 lab duplicate pairs	11 lab duplicate pairs	3% (6)	0.5% (1)
FFD, Failed Field Duplicate	28 field duplicate groups	30 field duplicate groups	10% (21)	9% (18)
FSL, Failed Lab Fortified Spike	19 lab fortified spike samples	25 lab fortified spike samples	16% (33)	19% (38)

Field blanks were analyzed to assess the potential for contamination of routine field samples. For total and dissolved mercury, a total of 36 blanks were analyzed, including 12 field reagent blanks, 12 field tubing blanks and 12 field filter blanks. Two field tubing blanks and one field reagent blank contained greater than 1 ng/L mercury and were flagged as contaminated according to the established MQOs. The maximum mercury concentration in these blanks was 1.2 ng/L. In addition, one other field reagent blank and associated field filter blank were flagged because the difference between these two blank concentrations and their associated field tubing blank was greater than 0.50 ng/L. In total, 14% of the blanks were flagged for contamination. However, because the blanks could not be associated with individual field samples, no field samples were flagged for blank failures. For methylmercury, no blank contamination flags were applied to the field samples. One field trip blank sample was analyzed, with a concentration of -0.0050 ng/L. Negative values are possible for methylmercury due to the analytical methodology, which involves the subtraction of results from two analytical steps.

Field and laboratory duplicate samples were analyzed to assess the precision of the measurement system. A total of 88 and 60 valid field duplicate samples were analyzed for mercury and methylmercury, respectively, including 2 cases where a methylmercury field sample had multiple duplicates. All field duplicate samples were classified as "sequential" because the duplicates were not collected within five minutes of the original sample due to equipment mobilization and sample pumping time. At least three sequential field duplicates were collected from each tributary for total and dissolved mercury analysis. For methylmercury analysis, at least one sequential field duplicate was collected from every tributary except for the Fox River. In accordance with the researcher's data qualifying rules for field duplicates, total and dissolved mercury samples were flagged for a failed field duplicate (FFD) based on a maximum relative percent difference (RPD) of 30% for samples greater than 5 times the method detection limit (MDL) and 50% for samples less than 5 times the MDL. A total of 9 dissolved mercury samples and 11 total mercury samples exceeded these maximum RPD limits. For methylmercury, a maximum RPD limit of 30% was used if all results were above 0.10 ng/L (approximately 5 times the MDL), and an absolute difference of 0.030 ng/L was used if at least one result was below 0.10 ng/L. These criteria were exceeded for 39 field duplicate pairs, however, only 8 of these pairs failed using the RPD criterion. The

remaining 31 pairs failed based on the absolute difference criterion, with the maximum absolute difference between duplicates equaling 1.1 ng/L.

For total and dissolved mercury analysis, at least one laboratory duplicate was prepared for all but 19 field samples. For some samples, multiple laboratory duplicates (up to 4) were prepared. Laboratory duplicates also were prepared for several field duplicate samples. For methylmercury analysis, laboratory duplicates were prepared for only 25 field samples, with no more than one laboratory duplicate prepared for a given sample. In accordance with the researcher's data qualifying rules for lab duplicates, total and dissolved mercury samples were flagged for a failed duplicate (FDL) based on a maximum RPD level (or RSD if more than one lab duplicate was analyzed for a given sample) of 20% for samples greater than 5 times the MDL and 50% for samples less than 5 times the MDL. A total of 15 dissolved and 6 total mercury sample pairs exceeded these maximum RPD/RSD criteria, with a maximum RPD/RSD of 80% calculated. For methylmercury, the rules for determining lab duplicate failure were the same as those used for determining field duplicate failure. These criteria were exceeded for 7 laboratory duplicate pairs. Three of these pairs failed using the RPD criterion and 4 pairs failed based on the absolute difference criterion. The maximum RPD measured for methylmercury samples was 107%, and the maximum absolute difference (between field sample and duplicate) was 0.34 ng/L.

To monitor the potential bias of analytical results, the laboratory prepared and analyzed a total of 162 laboratory fortified spike samples (LSFs). Samples were flagged for a failed lab fortified spiked sample (FSL) if the associated spike recovery was below 70% or above 130%. The FSL flag was applied to 1% of the total and dissolved mercury samples, due to two recoveries below the lower limit, with a minimum of 66%, and three recoveries above the upper limit, with a maximum of 159%. The FSL flag was applied to 16% of dissolved methylmercury and 19% of total methylmercury samples, due to one recovery below the lower limit (69%) and four above the upper limit, with a maximum of 153%. Based on analysis of laboratory spikes, blank contamination, and other internal QC data, the QC coordinator did not qualify any samples as high or low biased.

As discussed in Section 1.5.5, MQOs were defined in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. GLNPO derived data quality assessments based on a subset of these attributes. For example, system precision was estimated as the mean RPD between the results for field duplicate pairs. Similarly, analytical precision was estimated as the mean RPD between the field sample and duplicate result for laboratory duplicate pairs. Tables 4-9 and 4-10 provide summaries of data quality assessments for several of these attributes for tributary mercury and methylmercury data, respectively. The results of laboratory and field duplicate samples revealed good system and analytical precision for total and dissolved mercury data when the results were above 5 times the given MDL. System precision was described by mean RPDs of 17% and 20% for dissolved and total field duplicate samples, respectively. Analytical precision was even greater, with RPDs as low as 7.5% and 5.1% for dissolved and total mercury samples, respectively. When results were less than 5 times the MDL, mean RPDs were much higher. For field duplicates, the mean RPD was 45% for the 7 dissolved duplicate pairs and 182% for the one total duplicate pair. For laboratory duplicates, the mean RPDs were 14% for dissolved mercury samples and 54% for total mercury samples.

Methylmercury results were less precise than total and dissolved mercury results. For results that were greater than 5 times the MDL, mean field duplicate RPDs were 47% for dissolved methylmercury and 27% for total methylmercury. Mean laboratory duplicate RPDs were 47% and 13% for dissolved and total methylmercury, respectively, when all results were above 5 times the MDL. When results were less than 5 times the MDL, mean field duplicate RPDs were 99% and 51% for dissolved and total methylmercury, respectively. Mean laboratory duplicate RPDs were 62% and 26% for dissolved and total methylmercury, respectively.

Analytical bias was evaluated by calculating the mean recovery of LSF samples. Results indicated very little overall bias for analytical results. The mean LSF recovery for total and dissolved mercury was 103%. For methylmercury, the mean LSF recovery for dissolved samples was 99%, and the mean LSF recovery for total methylmercury was 110%.

Analytical sensitivity was evaluated by calculating the percentage of samples reported below the corresponding MDL (0.10 ng/L for total and dissolved mercury, and 0.019 ng/L for total and dissolved methylmercury). Only one dissolved mercury sample, or 0.3% of the data, and no total mercury samples, were below the detection limit for total mercury. For methylmercury, 31 dissolved samples (15% of the data) and 6 total samples (3% of the data) were below the MDL. Results from these samples were not censored and were used as reported in the analysis of tributary mercury data presented in this report.

Table 4-9. Data Quality Assessment for Mercury Data from Lake Michigan Tributaries

Parameter	Assessment[a]	
	Dissolved	Total
Number of Routine Samples Analyzed	346	353
Number of Sequential Field Duplicates Analyzed	49	49
System Precision, Mean Field Duplicate RPD (%), < 5*MDL	45% (7)	182% (1)
System Precision, Mean Field Duplicate RPD (%), > 5*MDL	17% (34)	20% (46)
Analytical Precision, Mean Lab Duplicate RPD (%), < 5*MDL	14% (29)[b]	54% (1)[b]
Analytical Precision, Mean Lab Duplicate RPD (%), > 5*MDL	7.5% (338)[b]	5.1% (381)[b]
Analytical Bias, Mean LFS (%)	103% (65)	103% (53)
Analytical Sensitivity, Samples reported as < MDL (%)	0%	0%

[a] Number of QC samples used in the assessment is provided in parentheses
[b] Includes laboratory duplicates of field duplicate samples
LFS = Laboratory Fortified Spike
MDL = Method Detection Limit

Table 4-10. Data Quality Assessment for Methylmercury Data from Lake Michigan Tributaries

Parameter	Assessment[a]	
	Dissolved	Total
Number of Routine Samples Analyzed	204	203
Number of Sequential Field Duplicate Groups Analyzed	28	30
System Precision, Mean Field Duplicate RPD (%), < MDL	99% (22)	51% (17)
System Precision, Mean Field Duplicate RPD (%), > MDL	47% (3)	27% (12)
Analytical Precision, Mean Lab Duplicate RPD (%), < MDL	62% (9)	26% (3)
Analytical Precision, Mean Lab Duplicate RPD (%), > MDL	47% (4)	13% (8)
Analytical Bias, Mean LFS (%)	99% (19)	110% (25)
Analytical Sensitivity, Samples reported as < MDL (%)	15%	3%

[a] Number of QC samples used in the assessment is provided in parentheses
LFS = Laboratory Fortified Spike
MDL = Method Detection Limit

4.3 Data Interpretation

4.3.1 Mercury Levels in Lake Michigan Tributaries

Total mercury concentrations in Lake Michigan tributaries averaged from 1.07 ng/L in the Muskegon River to 28.9 ng/L in the Fox River. Following the Fox River, the Kalamazoo and Grand Calumet Rivers averaged approximately 10 ng/L in total mercury. The remaining tributaries averaged from 1 to 6 ng/L in total mercury. These mercury levels are comparable to mercury concentrations measured in other Midwestern tributaries. In a survey of 39 Wisconsin rivers, Hurley *et al.* (1995) measured a mean total mercury concentration of 7.94 ng/L during the spring and 3.45 ng/L during the fall. This is consistent with LMMB Study data, where a majority of tributaries averaged between 3 and 7 ng/L total mercury. Similarly, Thompson-Roberts *et al.* (1999), measured average total mercury concentrations of 3 to 19 ng/L in 23 wetlands of the St. Lawrence River. Balogh *et al.* (1998) reported total mercury concentrations below 4 ng/L in the St. Croix River, below 10 ng/L in the headwaters of the Mississippi River, and routinely above 10 ng/L in the Minnesota River. In a summary of surface water mercury levels nationwide, USEPA (1997c) reported that total mercury levels in lakes and streams are typically well under 20 ng/L, however, elevated levels may be found in lakes and streams thought to be impacted by anthropogenic mercury sources. This is consistent with the results of this study, where all tributaries except for the Fox River were below 20 ng/L, and the Fox River is suspected of being impacted by resuspension of contaminated sediments from legacy sources (Hurley *et al.*, 1998a).

4.3.2 Comparison to Regulatory Limits

The average concentrations of mercury in Lake Michigan tributaries were all below EPA's nationwide freshwater water quality criterion for human health protection of 50 ng/L, and only the Fox River exceeded the chronic water quality criterion for protection of aquatic life (12 ng/L). When compared to the more stringent water quality criteria recommended for Great Lakes states, three tributaries exceed the Great Lakes water quality criterion for human health (1.8 ng/L dissolved mercury) and eight tributaries exceed the Great Lakes water quality criterion for wildlife (1.3 ng/L dissolved mercury). The Fox, Manistique, and Menominee Rivers exceed the human health criterion, and all tributaries except for the Muskegon, Milwaukee, and Grand Calumet Rivers exceed the wildlife criterion.

4.3.3 Seasonality

While tributaries differed in their seasonal patterns of flow and mercury concentrations, many of the Lake Michigan tributaries exhibited significantly lower mercury concentrations during the winter and higher mercury concentrations in conjunction with spring high-flow conditions or event flows during the summer and fall. Balogh *et al.* (1998) similarly found that total mercury concentrations in the Minnesota, St. Croix, and Mississippi Rivers varied seasonally with lowest levels during the winter, increasing concentrations during spring runoff, and fluctuating concentrations throughout the spring, summer, and fall in response to precipitation runoff events. In the Minnesota River, Balogh *et al.* (1997) reported total mercury concentrations from less than 1.0 ng/L during the winter months to greater than 35 ng/L following spring runoff. When comparing just spring and fall concentrations, Hurley *et al.* (1995) found strong seasonal variability in 39 Wisconsin Rivers, with total mercury concentrations approximately two times higher in the spring than in the fall.

In tributaries that are dominated by particulate mercury, lower total mercury concentrations during the winter are tied to lower suspended solids concentrations during the winter. The low-flow conditions that occur during the winter in conjunction with the ice cover that forms over many Lake Michigan tributaries contribute to reduced turbulence and reduced sediment resuspension. This reduced suspended sediment load during the winter decreases particulate, and therefore total, mercury concentrations in the water

column (Hurley *et al.*, 1998a). This conclusion is consistent with correlations of total mercury with particulate organic carbon concentrations, total solids concentrations, and suspended particulate matter identified in this and other studies (Hurley *et al.*, 1998a; Balogh *et al.*, 1998; Balogh *et al.*, 1997).

Seasonal differences in the fluxes of mercury from Lake Michigan tributaries were even more apparent than seasonal differences in mercury concentrations alone. Hurley *et al.* (1998b) investigated the fluxes of mercury from Lake Michigan tributaries during three flow regimes: spring, base flow, and event. For all tributaries except the Grand Calumet, base flow fluxes were considerably lower than fluxes during either spring or event conditions. In comparing spring and event fluxes, Hurley *et al.* (1998b) found that the patterns of mercury flux and flow regimes differed among the tributaries. In the Fox, St. Joseph, and Manistique Rivers, fluxes associated with the spring flows were much greater than those associated with summer and fall events. In contrast, mercury fluxes in the Grand and Kalamazoo Rivers were greater during summer and fall events than during spring flows. These differences were explained in part by differences in watershed land use patterns (Hurley *et al.*, 1998b). The Grand and Kalamazoo River watersheds contain significant agricultural land cover with increased particulate erosion susceptibility during precipitation events.

4.3.4 Regional Considerations

Of the 11 Lake Michigan tributaries evaluated in the LMMB Study, total mercury concentrations were highest in the Fox River. Average total mercury concentrations in the Fox River were 2.7 times higher than in any other tributary. The maximum total mercury concentration of 191 ng/L measured in the Fox River was more than four times higher than the maximum concentration measured in any other tributary. Following the Fox River, total mercury concentrations were highest in the Grand Calumet and Kalamazoo Rivers. Total mercury concentrations in these two rivers were significantly higher than in any other tributary, except for the Fox River. Each of these rivers (the Fox, Grand Calumet, and Kalamazoo) have significantly urbanized and industrialized watersheds, which suggests anthropogenic sources. In more intensive surveys of the lower Fox River that included longitudinal transect sampling and analysis of sediment cores, Hurley *et al.* (1998a) concluded that mercury enrichment in the Fox River was due to resuspension of historically contaminated sediments. Mercury concentrations of up to 5.69 µg/g in deeper sediment cores (18-cm composites) in conjunction with scouring from high flow events were sufficient to produce the water column mercury levels measured at the mouth of the Fox River. Hurley *et al.* (1998b) also measured mercury levels in the suspended particulate matter on a ng/g basis and concluded that the Fox and Grand Calumet Rivers contained particles that were highly enriched with mercury compared to the other tributaries. Levels of mercury in particles from the remaining tributaries were generally 50 to 200 ng/g and in the range reported for Midwestern soils.

While the highest total mercury concentrations were observed in urban and industrial watersheds, the lowest total mercury concentrations were observed in predominantly forested and wetland watersheds. The more-northern Muskegon, Manistique, Pere Marquette, and Menominee Rivers contained the lowest total mercury concentrations, averaging only 1.07 to 3.63 ng/L. Hurley *et al.* (1995) also found that mercury yields varied by watershed land use patterns in 39 Wisconsin rivers. Mean spring concentrations and yields of mercury were highest in urban watersheds, followed by wetland and forest watershed, with lowest values in agricultural watersheds.

4.3.5 Mercury Fractions and Forms

Tributaries also differed in the fractions and forms of mercury present. In each of the three most mercury-contaminated tributaries (Fox, Grand Calumet, and Kalamazoo Rivers), mercury was predominantly in the particulate fraction. Particulate mercury accounted for 85%, 92%, and 81% of total mercury in the Fox, Grand Calumet, and Kalamazoo Rivers, respectively. In the least contaminated

tributaries (the Muskegon, Manistique, Pere Marquette, and Menominee Rivers), total mercury concentrations were dominated by the dissolved fraction. The dissolved fraction accounted for 54% to 99% of total mercury in these tributaries. In fact, the Manistique, Menominee, and Pere Marquette Rivers contained the second, third, and fourth highest average dissolved mercury concentrations. Hurley *et al.* (1998b), however, notes that on a flux basis, inputs of dissolved mercury from the Fox, Kalamazoo, Grand, and St. Joseph Rivers are of the same magnitude as those from the dissolved mercury-dominated tributaries.

Balogh *et al.* (1998) found similar results when investigating mercury in diverse Minnesota river basins. In the more forested and wetland-dominated watershed of the St. Croix River, the dissolved fraction dominated mercury mobility, while the particulate fraction dominated mercury mobility in the agricultural Minnesota River watershed. Dissolved mercury accounted for over 62% of the total mercury in the St. Croix River and less than 10% of the total mercury in the Minnesota River. Likewise, wetland/forest watersheds in Wisconsin were dominated by mercury fluxes in the filtered fraction, while agricultural watersheds were dominated by mercury fluxes in the particulate fraction (Hurley *et al.*, 1995).

With the exception of the Muskegon River (where methylmercury accounted for 21% of total mercury), methylmercury accounted for only 0.48% to 5.9% of total mercury in Lake Michigan tributaries. In a study of 39 Wisconsin rivers, Hurley *et al.* (1995) similarly found that methylmercury accounted for an average of less than 2.2% to 6.4% of total mercury. Lake Michigan tributaries such as the Fox, Grand Calumet, and Kalamazoo Rivers that had the highest total mercury concentrations did not have correspondingly high methylmercury concentrations. These tributaries ranked fifth, sixth, and tenth in total methylmercury concentrations among the tributaries. Hurley *et al.* (1998b) cautioned, however, that just because those sites with high total mercury levels contained only a small portion of mercury in more bioavailable dissolved and methyl forms, these loads should not be discounted as inert. These particulate-bound contaminants can be deposited in Lake Michigan sediments and undergo methylation, reintroducing biologically available mercury to the Lake Michigan system.